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PROCESSES OCCURRING IN SYNTHESIS OF IRON-BEARING GLAZE FRITS

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The authors consider the processes of silicate and glass formation in iron-containing glass batches based on technical materials (oxides and carbonates) and using magma rock (metadiabase). The specific features of these processes depending on the chemical composition of glass are identified. It is established that the crystalline phases arising in silicate formation persist in the glass melt in the form of structural groups. The possibility of decreasing the temperature of glaze-frit synthesis in the case of using metadiabase is considered.

A current goal of the ceramic industry consists of involving available natural resources and various kinds of industrial waste in ceramic production. In certain cases, the quality of products based on these materials exceeds the quality of products made of expensive synthesized materials. Such resources include rocks of the basic composition, namely, metadiabases [1, 2] containing an elevated amount of colorant iron oxides and also alkaline and alkaline-earth metal oxides, which can be used to produce pigment-free colored glazes of a wide color range.

The synthesis of tinted glazes based on natural magma materials has not been systematically investigated, and there is a lack of theoretical analysis of the phase formation in iron-bearing silicate systems (staring with solid-phase reactions in batches and ending with the structural transformations in the melt and in the emerging glaze coatings). The na-

ture and degree of completion of the silicate- and glass-formation processes in a glass batch to a great extent determine the properties and the phase composition of the glaze, as well as its fritting and fusion temperatures. It is known [3] that vitrification processes in iron-bearing mixtures occur at lower temperatures due to the strength of the Fe – O bond being lower than that of the Si – O bond, the incorporation of Fe_2O_3 in the structural lattice of glass in the form of tetrahedrons $[FeO_4]^{2-}$, and the modifying role of the bivalent iron ion. Moreover, there exists a hypothesis [4] that the crystal phases emerging as the result of silicate formation persist in the melt and in the glass in the form of structural groups, which contributes to decreasing the temperature and increasing the intensity of the formation of the respective phases in the glaze coating.

In this context, the study of the processes of silicate and glass formation in iron-bearing batches is of certain interest. In order to identify the specifics of these processes, when the batch contains metadiabase, a comparative study was simultaneously performed on model batches based on technical raw materials, i.e., oxides and carbonates. The compositions of the considered batches and the chemical composition of glasses are given in Tables 1 and 2.

The study was carried out by an integrated method including differential thermal and x-ray phase analysis, as well as IR spectroscopy.
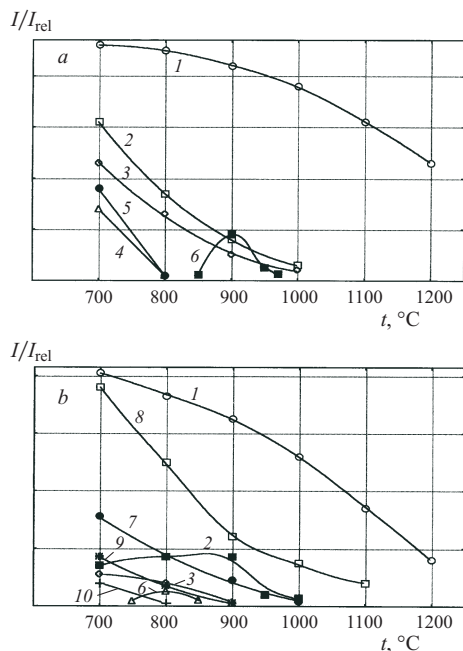
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TABLE 1

Batch	Weight content, %				
	metadiabase	quartz sand	boric acid	soda ash	natural chalk
6.1	45.90	15.15	65.00	12.83	–
12.2	68.85	12.63	10.00	17.10	8.90

TABLE 2

Glass	Weight content, %										
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	B_2O_3
6.1	35.54	0.54	8.20	2.54	2.43	0.07	1.94	3.90	11.56	0.77	32.50
12.2	47.24	0.81	12.21	3.81	3.64	0.11	2.88	10.82	12.33	1.15	5.00

Fig. 1. Modification of the phase composition of model (*a*) and synthesized (*b*) batches of composition 6.1 in melting: *1*) quartz, *2*) hematite; *3*) magnoferrite; *4*) scorlomite; *5*) aegirite-augite; *6*) sodium-magnesium silicate; *7*) amphibole; *8*) plagioclase; *9*) biotite; *10*) epidote.

The DTA of the batches revealed the existence of three endothermic effects in the temperature range $640 - 840°C$, which is usually attributed to decomposition of carbonates, the silicate formation reactions, and melting of eutectic series. The first two effects in metadiabase-containing batches are less intense, whereas the latter effect determined by the reaction between free soda and silica and the emergence of the liquid phase clearly exhibits a trend to shifting toward a lower temperature range $(760 - 780°C)$. This can be accounted for by the fact that natural silicates are introduced into the batch composition via metadiabase, whereas the formation of silicates in a model batch requires a certain heat consumption. There are also reasons for believing that when natural silicates are introduced, the eutectics are formed much more easily, and, accordingly, the total heat consumption in frit melting decreases. Furthermore, the use of rocks containing silicate and aluminate compounds, in which the iron ions predominantly exist in the bivalent state, helps to prevent intense foaming at the melting stage [5], which was indeed observed in our experiments.

The phase composition of the products of heat treatment of batches in the temperature interval $700 - 1200°C$ was studied on a DRON-3 diffractometer (FeK$_\alpha$ radiation).

At 700°C the diffraction pattern of model batch 6.1 (Fig. 1) clearly manifests diffraction maximums belonging to quartz and hematite. The presence of α-Al$_2$O$_3$ is identified, which is evidence of the incomplete reaction of aluminum oxide at the specified temperature. Another product is spinel,

i.e., magnoferrite MgFe$_2$O$_4$, whose formation is determined by the emergence of MgO at the early stage of heat treatment due to the decomposition of magnesium carbonate and its reaction with α-Fe$_2$O$_3$. Two ternary compounds are identified among the product of the batch heat treatment at the specified temperature. They are calcium-ferrous silicate, in which a part of the Fe^{3+} and Si^{4+} ions has been isomorphically replaced with titanium ions with the formation of scorlomite Ca$_3$(Fe, Ti)$_2$(Si, Ti)$_3$O$_{12}$, and pyroxene silicate of the aegirite-augite composition (Ca, Na)(Fe^{2+}, Mg^{2+}, Fe^{3+})Si$_2$O$_6$.

As the heat-treatment temperature increases to 800°C, the peaks related to α-SiO$_2$, α-Fe$_2$O$_3$, and MgFe$_2$O$_4$ become less intense, which reflects the transition of these phases into the melt. Judging from the peak shapes, the phases of scorlomite and aegirite-augite are absent, i.e., these phases are intermediate products of the batch-component reactions.

At a temperature of 900°C, the transition of α-SiO$_2$, α-Fe$_2$O$_3$, and MgFe$_2$O$_4$ into the melt continues. At 1000°C, the residual reflections of α-Fe$_2$O$_3$ and MgFe$_2$O$_4$ are registered in the diffraction pattern. Owing to the melt saturation with magnesium oxides in melting of MgFe$_2$O$_4$, the existence of sodium-magnesium silicate is registered within the temperature interval $850 - 950°C$ The complete melting of the batch components and the products of silicate formation occurs at 1280°C.

At 700°C, batch 6.1 based on metadiabase exhibits the following phases corresponding to the rock-forming metadiabase minerals: hornblende (the amphibole group), oligoclase-andesine (plagioclase), biotite, magnetite, and epidote, as well as quartz. In addition to that, hematite and magnoferrite are present as well; their formation is determined by the oxidation of structural iron in hornblende and partial decomposition of epidote and biotite. With increasing temperature, the rock-forming minerals and the batch components melt. An increase in the quantity of hematite is registered up to 900°C with its subsequent melting on a further temperature increase. Sodium-magnesium silicate, which is registered in the model batch, in this particular batch is formed in a small amount at a temperature of 800°C.

It is established that melting of metadiabase components in glass batches occurs more intensely and at lower temperatures compared to natural metadiabase. Thus, the destruction of epidote occurs up to 800°C, intense decomposition of amphibole is registered within the interval $800 - 1000°C$, and decomposition of biotite up to 900°C. Moreover, in the batch of this particular composition, the pyroxene phases are not formed from the products of decomposition of the rock-forming minerals, as typically happens in natural metadiabase, which can be attributed to the emergence of a significant amount of the liquid phase at a low temperature. The vitrification processes in the metadiabase-bearing batch are more intense and shifted toward the low-temperature region by about $40 - 60°C$ compared to the model batch. Complete melting of the batch components is observed at $1220 - 1240°C$.

A similar study of the processes of glass and silicate formation was performed on batch 12.2, which differed from batch 6.1 not only in an additional content of CaO introduced via $CaCO_3$, but also in a higher content of metadiabase at the expense of a decreased B_2O_3 content. Accordingly, one could expect modifications in the glass- and silicate-formation processes in batch 12.2.

The phase composition of the heat-treatment products of model batch 12.2 (Fig. 2) at 700°C is similar to batch 6.1 and is represented by α-SiO_2, hematite, magnoferrite, residual non-reacting α-Al_2O_3, and also scorlomite and aegirite-augite. An increase in the temperature facilitates the dissolution of quartz. At 800°C, the scorlomite phase is absent. In contrast to batch 6.1, the peaks related to aegirite-augite at the given temperature are more intense. The temperature interval of the existence of this phase continues up to 850°C. Moreover, a compound of the composition $Na_2O \cdot 2CaO \cdot Al_2O_3 \cdot 4SiO_2$ was registered, which belongs to the silicates with separate $[Si_2O_7]$ groups (the melilite group). The highest intensity in the peaks of this phase is registered at 1000°C, and at temperatures above 1000°C this phase transforms into the melt.

At 900°C, sodium-aluminosilicate $NaAlSiO_4$ is formed in the heat-treatment products of the model batch, and its quantity increases up to 1050°C. The dissolution of quartz, hematite, and magnoferrite becomes more intense. The formation of a diopside-like solid phase is registered at 1000°C.

The phase composition of the batch sinter at 1100°C is represented by quartz, the diopside phase, and sodium aluminosilicate, whereas at 1200°C only quartz is present. The complete melting of the batch is registered at 1300°C.

The x-ray pattern of glass batch 12.2 based on metadiabase exhibits at 700°C the diffraction maximums related to plagioclase, amphibole, biotite, epidote, hematite, quartz, magnetite, and magnoferrite. Magnoferrite is formed as a consequence of magnetite decomposition.

At 800°C, the intensity of the peaks of all earlier existing phases diminishes. Epidote is not registered at this temperature. Biotite is destroyed within the temperature interval between 700 and 1100°C. The process starts at 750°C, whereas the decomposition products form magnoferrite, which is evidenced by the increasing peaks of this phase up to 1000°C. Moreover, the amount of hematite, which emerges in destruction of amphibole, increases. Simultaneously with the specified processes, the melilite phase is formed, and the peaks typical of the diopside-like phase emerge.

At 900°C, an increase in the maximums related to spinels (magnetite and magnoferrite), melilite, and the diopside phase is registered in the products of heat treatment, which is presumably due to the decomposition of the rock-forming amphibole and biotite, as well as melting of plagioclase and the batch components. Melilite melts with increasing temperature, and only traces of this phase are seen at 1000°C.

The intense decomposition of amphibole is registered within the temperature interval 950 – 1050°C, which is 50 – 100°C lower than in pure metadiabase. At the same
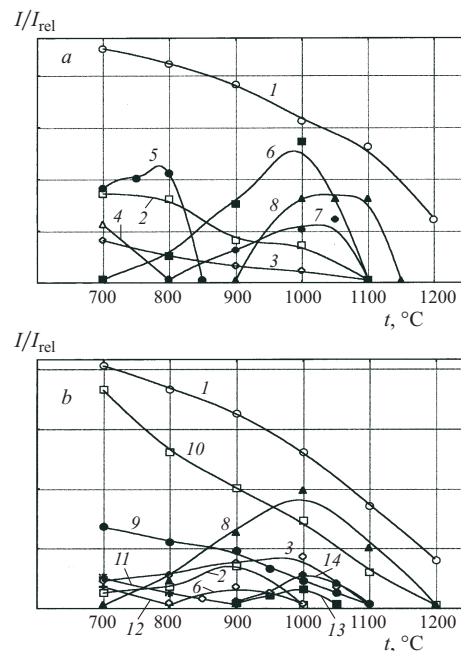

Fig. 2. Modification of the phase composition of model (*a*) and synthesized (*b*) batches of composition 12.2 in melting: *1*) quartz, *2*) hematite; *3*) magnoferrite; *4*) scorlomite; *5*) aegirite-augite; *6*) melilite; *7*) sodium aluminosilicate; *8*) diopside; *9*) amphibole; *10*) plagioclase; *11*) biotite; *12*) epidote; *13*) hypersthene; *14*) spinel.
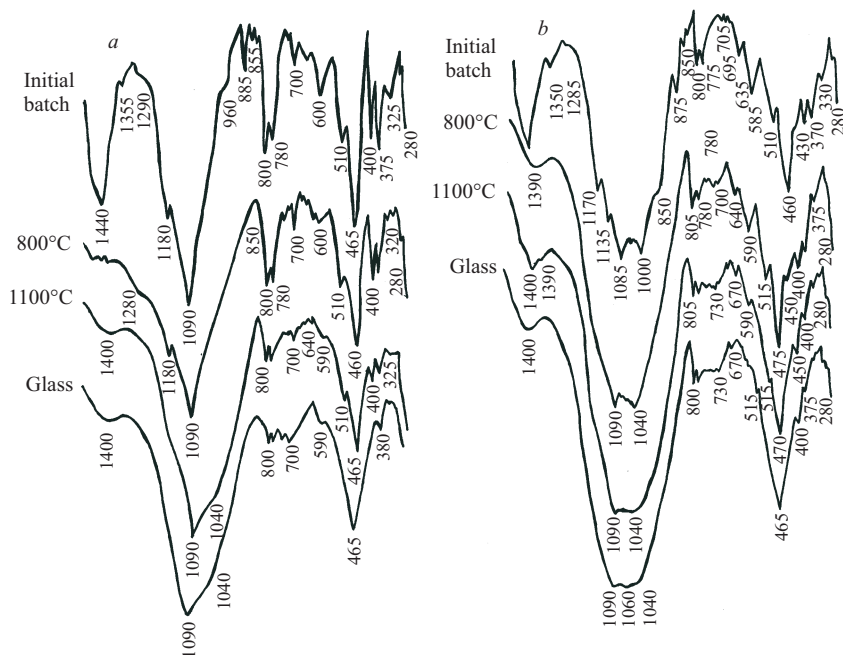
time, a diopside-like phase, whose peak intensities are significant at 1000°C, and hypersthene $(Fe, Mg)SiO_3$, which is a solid solution of $FeSiO_3$ and $MgSiO_3$, are formed. The intense formation of $MgFeAlO_4$ (a compound with a spinel structure) is registered at 1000°C; traces of this compound are already observed at 900°C, and at a temperature above 1100°C $MgFeAlO_4$ transforms to the melt.

Note that the intensity of the hematite peaks decreases at 1000°C, and at 1100°C hematite is absent, i.e., Fe_2O_3 either passes over to the melt or reacts with the batch components forming magnetite and magnoferrite.

At 1100°C, the intensity of all peaks decreases, since virtually all phases pass into the melt. The pattern exhibits the diffraction maximums of quartz and the residual reflections of the plagioclase and diopside phases, hypersthene and $MgFeAlO_4$. The x-ray pattern of the heat-treatment products of the batch at 1200°C exhibits only α-SiO_2 peaks of insignificant intensity.

Thus, as batch 12.2 is heated, along with dissociation of single components and formation of a number of reaction products, the intense formation of the diopside-like phase is observed. The full melting of this batch is observed at 1240 – 1250°C, which is significantly lower than the melting temperature of the model batch of the same composition.

To refine the obtained data, the structural modifications in the batch reaction products and glasses were studied using IR spectroscopy. Owing to the multicomponent composition of the glass batches and the interference of absorption bands

Fig. 3. IR spectra of model (*a*) and synthesized (*b*) batches and glasses of composition 12.2.

It is more difficult to analyze the main band region of $280 - 450 \text{ cm}^{-1}$, in which bands $[SiO_4]$ and bands $[MeO_6]$ interfere. The absorption band for group $[Fe^{2+}O_6]$ lies in the range $300 - 400 \text{ cm}^{-1}$, and the band for groups $[Fe^{3+}O_6]$ is within the range of around 320 cm^{-1}.

As a consequence of the studies performed, it was established that the modifications in the IR absorption spectra of both model and metadiabase-bearing batches support the x-ray analysis data. As the temperature in the model batches increases, the main band expands toward lower frequencies, which is caused by the formation of Si – O – Si groups of the disilicate (laminar structure) and metasilicate (chain-ribbon structure) types, as well as ring-shaped and insular groups, whose absorption bands were registered in the range $740 - 830 \text{ cm}^{-1}$. The depolymerization of Si – O – Si bonds with increasing temperature was registered as well in the metadiabase-containing batch. As the temperature of heat treatment increases, a smoother spectrum with less intense absorption bands points to the transition of the batch components to the vitreous state. A decrease in the band intensity in the range $780 - 800 \text{ cm}^{-1}$ points to the conversion of the quartz grains to the vitreous phase.

The modifications of the IR spectra of the batch heat-treatment products suggest that the structural groups that have been formed in the course of the solid-phase reactions in the batch persist in the melt as well, having various degrees of dissociation, depending on the melt temperature. Moreover, as the melt cools, these structural groups appear to polymerize. This creates the conditions for fast nucleation of crystalline centers during the firing of coatings and lowers the temperature of crystal-phase formation.

The results of the x-ray phase analysis and IR spectroscopy indicate that the dissolution of quartz grains in the model and metadiabase-containing batches differs in its intensity and temperature interval. It is known that the process of dissolution of residual quartz grains is limited by the diffusion of excessive SiO_2 from the boundary zone oversaturated with silicon dioxide into the surrounding silicate solution under the effect of the concentration gradient. In using metadiabase-bearing batches, the liquid phase, which emerges in a significant quantity at low temperatures, facilitates the intense dissolution of the batch components, which increases the rate of dissolution of the quartz grains at the stage of vitrification. Furthermore, the major part of SiO_2 is incorporated in the structure of the rock-forming minerals and transforms to the melt in melting of these minerals, whereas at the stage of vitrification only the quartz grains introduced via quartz sand are dissolved. All this determines the lower tem-

typical of various batch components and reaction products, the resulting spectrograms are very complicated (Fig. 3). The main difference between the spectra of model and metadiabase-bearing batches and glasses is observed in the range of the stretching vibrations of Si – O bonds, which is caused by the different degree of cohesion in $[SiO_4]$ tetrahedrons. The model batches exhibit a narrow intense band with a maximum at 1090 cm^{-1}, which corresponds to the vibrations of Si – O bonds in the quartz structure. The band of the main stretching vibrations of Si – O bonds in the metadiabase-bearing batch has a significant width and encompasses the range from 800 to 1150 cm^{-1} with maximums at 1090, 1040, and $960 - 1000 \text{ cm}^{-1}$, which correlates with the stretching vibrations of Si – O – Si bonds, respectively, in the skeleton structure of plagioclase and in the laminar and chain-like amphibole structures [6].

Amphiboles also have intense bands in the range of $920 - 940$ and $630 - 650 \text{ cm}^{-1}$. The IR spectra do not exhibit "pure" $Me^{2+} - O$ and $Me^{3+} - O$ absorption spectra, which is due to the effect of the powerful charge and the polarizing effect of silicon ions, as Me^{2+} and Me^{3+} ions in octahedral positions share easily polarized oxygen ions with silicon ions [6, 7]. However, combined bands Si – O – Me^{2+} and Si – O – Me^{3+} can be identified. The bands in the range $470 - 550 \text{ cm}^{-1}$ relate to the vibrations of Si – O – Me^{3+} bonds. The bands related to Si – O – Me^{2+} bonds, owing to a greater distance $Me^{2+} - (O - Si)$ and the more ionic type of this bond, are registered at lower frequencies ($400 - 450 \text{ cm}^{-1}$).

perature of glass synthesis, when metadiabase is used in the batch composition.

Thus, the studies performed determined the specifics of the physicochemical processes occurring in heating the model and the metadiabase-bearing glass batches. The observed distinctions in the modification of the phase composition in glass batches are primarily determined by the phase composition and structure of the metadiabase. The silicate-formation processes coincide with the emergence of compounds in melting and dissociation of the rock-forming minerals. Furthermore, in metadiabase melting the rock-forming minerals persist as structural groups preserving the near order in the melt and having various degrees of dissociation, depending on the melt temperature, which also determines the distinctions in the physicochemical processes expressed in the formation of the spinel phases and pyroxenes (hypersthene and diopside).

The dissociation of single components and formation of the products of component reactions in the low-boron calcium-containing batch 12.2 is accompanied by intense formation of the diopside-like phases. The emergence of the solid diopside solution in the metadiabase-bearing batch is determined by the presence in the melt of structural groups typical of pyroxenes, which are formed in the decomposition of rock-forming minerals (amphiboles). The diopside phase presumably emerges in the model batch as a result of the formation of the aegirite-augite solid solution and its subsequent transformation into the diopside composition.

The presence of a significant quantity of boron-bearing material in batch 6.1 causes significant modifications in the silicate-formation process. Moreover, the insignificant quantity of CaO decreases the number of possible reactions with its participation, which decreases the probability of the formation of calcium compounds. It is probable that soda in the high-boron batch does not react with SiO_2 (eutectic at 780°C)

but reacts with boron oxide. In this case, sodium borate is formed, which later in the interval of 600 – 1200°C actively dissolves the batch components. The silicate-formation reactions in this case either do not take place or proceed at a low rate. The solid solution of diopside is not formed in this batch, which is further evidence of the high dissolving capacity of the emerging melt. The main reactions in the high-boron batches are the reactions with the participation of iron, sodium, and magnesium oxides, namely, the formation of sodium-magnesium silicate, solid solution of aegirite-augite, and also magnoferrite and magnetite.

These studies of the physicochemical processes occurring in iron-bearing glass batches, both model ones and batches using metadiabase, open up possibilities for controlling the process of melting iron-containing glasses and using various types of iron-bearing materials in production.

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